

CLAIMS

1. A method of conditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina, the metallic anode structure having initially an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds, in particular oxides and fluorides, of metals from the metallic anode structure, the method comprising the steps of:
  - 10 a) substantially preventing the essentially metallic active surface free of said ceramic compound from reacting with any reactable species, in particular oxygen and fluorine species, until immersion into a molten electrolyte containing oxygen ions;
  - 15 b) immersing into the molten electrolyte the metallic anode structure with its essentially metallic active surface free of said ceramic compounds; and
  - 20 c) polarising the immersed metallic anode structure to form thereon a dense and coherent integral iron-based oxide layer which is electrochemically active for the oxidation of oxygen and which inhibits diffusion of oxygen towards the metallic anode structure.
2. The method of claim 1, wherein prior to immersion, the metallic anode structure is pre-heated with its essentially metallic active surface maintained free of said ceramic compounds.
3. The method of claim 1 or 2, wherein prior to immersion into the molten electrolyte the active surface is covered with a temporary protective layer which is substantially impermeable to any species reactable with the active surface and which is removed prior to immersion into the molten electrolyte or by contact with the molten electrolyte.
4. The method of claim 3, wherein the protective layer is heat stable.

5. The method of any preceding claim, wherein prior to immersion, the metallic anode structure is pre-heated in an atmosphere that is substantially free of any species reactable with the active surface.

5 6. The method of any preceding claim, wherein the iron-based alloy outer part comprises nickel and/or cobalt.

7. The method of any preceding claim, wherein the iron-based alloy outer part comprises one or more elements selected from copper, molybdenum, manganese, titanium, 10 tantalum, tungsten, hafnium, vanadium, zirconium, niobium, chromium, cobalt, aluminium, silicon, carbon and the rare earth metals, in particular yttrium.

8. The method of claim 5, wherein the iron-based alloy outer part, consists essentially of:

15 - 45-55 weight% iron;  
- 15-55 weight% in total of nickel and/or cobalt;  
- 0-30 weight% copper; and  
- 0-10 weight% in total of one or more further elements.

20 9. The method of any preceding claim, wherein the metallic anode structure is a cast alloy.

10. The method of claim 9, wherein the metallic anode structure is quenched prior to immersion into the molten electrolyte.

25 11. The method of claim 9 or 10, wherein the metallic anode structure is subjected to an annealing heat treatment prior to immersion into the molten electrolyte.

30 12. A method of conditioning or reconditioning a metallic anode structure for producing aluminium in a molten electrolyte containing dissolved alumina, the metallic anode structure comprising an iron-based alloy outer part having a surface which is covered with ceramic compounds, in particular oxides and fluorides, of metals from the outer part, said method comprising the steps of:

- removing substantially all ceramic compounds from the surface of the outer part to form an essentially metallic active anode surface; and then
- conditioning according to any preceding claim the metallic anode structure with its essentially metallic active anode surface free of any ceramic compounds.

5 13. A method of electrowinning aluminium comprising the steps of:

- conditioning according to any preceding claim a metallic anode structure including the step of polarising in a molten electrolyte to form on the anode structure a dense and coherent integral iron-based oxide layer; and
- electrolysing dissolved alumina in the same or a different molten electrolyte using the conditioned anode structure to evolve oxygen thereon and produce aluminium on a facing cathode.

10 14. The method of claim 13, wherein the dense and coherent integral iron-based oxide layer formed by said polarising step of the conditioning is further formed during electrolysis by slow oxidation of the metallic anode structure at the metallic structure/oxide layer interface.

15 15. The method of claim 14, wherein constituents of the dense and coherent integral iron-based oxide layer slowly dissolve into the electrolyte during electrolysis, preferably at a rate corresponding to the oxidation rate of the metallic anode structure.

20 16. The method of claim 13 or 14, comprising maintaining in the aluminium-production molten electrolyte an amount of dissolved iron species and dissolved alumina sufficient to inhibit significantly dissolution of constituents of the dense and coherent integral iron-based oxide layer.

25 17. The method of any one of claims 13 to 16, comprising maintaining the aluminium-production molten electrolyte at

a temperature below 960°C, preferably between 840°C and 940°C.

18. The method of any one of claims 13 or 17, wherein the aluminium production molten electrolyte contains NaF and 5 AlF<sub>3</sub> in a molar ratio in the range from 1.2 to 2.4.

19. The method of any one of claims 13 to 18, wherein the concentration of alumina dissolved in the aluminium production molten electrolyte is below 10 weight%, preferably between 5 weight% and 8 weight%.

10 20. The method of any one of claims 13 to 19, wherein alumina-depleted electrolyte is circulated away from the electrochemically active iron-based oxide layer, enriched with alumina, and alumina-enriched electrolyte is circulated towards the electrochemically active iron-based 15 oxide layer.

21. An aluminium electrowinning anode structure comprising an iron-based alloy metallic outer part covered with a dense and coherent integral iron-based oxide layer obtainable by conditioning according to any one of claims 20 1 to 10 a metallic anode structure having an iron-based alloy outer part with an active anode surface which is essentially metallic and free of any ceramic compounds of metals from the metallic anode structure.

25 22. An aluminium electrowinning anode structure comprising an iron-based alloy metallic outer part with an active anode surface which is essentially metallic and free of any ceramic compounds of metals from the metallic anode structure and which is covered with a temporary protection medium that substantially prevents ceramic-forming reactions at the essentially metallic anode 30 surface, which medium is separable from the active surface prior to or upon immersion into the molten electrolyte.

35 23. The anode structure of claim 22, wherein the temporary protection medium is removable prior to immersion into the electrolyte.

24. The anode structure of claim 22 or 23, wherein the temporary protection is soluble in the electrolyte.
25. The anode structure of any one of claims 22 to 24, wherein the temporary protection medium comprises one or 5 more solid layers.
26. The anode structure of claim 25, wherein at least one solid layer comprises a ceramic, such as alumina.
27. The anode structure of claim 25 or 26, wherein at 10 least one solid layer comprises a metal, in particular a reactable metal, such as aluminium, iron, copper, chromium or yttrium, for reacting with possibly diffusing reactive gases.
28. The anode structure of any one of claims 25 to 27, wherein at least one solid layer comprises a polymer.
- 15 29. The anode structure of claim 28, which is wrapped under vacuum or inert gas in the solid polymer layer.
30. The anode structure of any one or claims 22 to 29, wherein the temporary protection medium comprises an inert liquid, such as oil or grease.
- 20 31. The anode structure of claim 22 to 30, wherein the temporary protection medium comprises an inert gas, such as nitrogen and/or carbon dioxide.
32. An aluminium electrowinning cell comprising at least one oxygen-evolving anode structure according to claim 21.
- 25 33. The cell of claim 32, comprising an aluminium-wettable cathode, in particular a drained cathode.